Chapter 5.5

Photochemical Reactions of Transition Metal Complexes Induced by Intramolecular Electron Transfer between Weakly Coupled Redox Centers

A. Vogler

1 INTRODUCTION

Light-induced electron transfer may take place as an inter- or intramolecular process. There is certainly no fundamental difference between both possibilities. However, intramolecular electron transfer is generally much better defined with regard to the geometrical arrangement of electron donor and acceptor. Unfortunately, the investigation of intramolecular light-induced electron transfer is hampered by other complications.

In most transition metal complexes the electronic interaction between metal and ligands cannot be neglected and may be rather strong. Consequently, intramolecular electron transfer involving metal and ligands takes place between coupled redox centers. In these cases it is often not quite clear what fraction of charge is transferred from the metal to the ligand and vice versa since donor and acceptor orbitals are delocalized to a certain degree. The majority of photoredox processes of metal complexes which have been reported (refs. 1-3) take place upon direct optical charge transfer (CT) excitation involving redox centers with substantial coupling. Although this review deals essentially only with systems consisting of weakly coupled donors and acceptors a short general survey of intramolecular optical CT excitation of transition metal complexes regardless of the extent of coupling is given here. CT transitions are classified according to the redox sites (ref. 4).

Ligand to Metal Charge Transfer (LMCT)

LMCT is a classical optical transition of metal complexes. Corresponding absorption bands are observed at low energies if the metal is oxidizing and the ligand reducing. Co(III) and Fe(III) complexes are well-documented examples. The colors of d^0 oxometallates such as the yellow CrO_4^{2-} and the violet MnO_4^- are caused by LMCT bands. In many cases LMCT excitation is associated with the reduction of the metal and oxidation of the ligand. Co(III) ammines undergo such photoredox reactions (refs. 1,2).

Metal to Ligand Charge Transfer (MLCT)

MLCT is another classical optical transition of metal complexes. MLCT absorption bands appear at long wavelength if the metal is reducing and a li-

gand provides low-energy empty orbitals. Complexes such as $[Fe(CN)_6]^{4-}$ and $[Ru(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridyl) are typical cases (ref. 4). In addition, organometallics which contain a metal in a low oxidation state and π-accepting ligands such as an olefin or an aromatic molecule are characterized by low-energy MLCT bands (ref. 3). Since metal ligand bonding is not much affected intramolecular photoreactions do generally not occur on MLCT excitation. Ligands are electron rich and cannot be easily reduced to stable species. MLCT excitation is therefore often associated with photooxidation of the metal while an electron is transferred from the ligand to another molecule by an intermolecular process. In the case of $[Fe(CN)_6]^{4-}$ the solvent may act as electron acceptor (ref. 2). In the MLCT state the ligand can be also susceptible to an electrophilic attack. The addition of protons to coordinated NO (ref. 5) or carbynes (ref. 6) illustrates this type of excited state reactivity.

Ligand to Ligand Charge Transfer (LLCT)

LLCT absorptions were observed only recently. These bands appear if one ligand is reducing and another oxidizing. LLCT bands were detected in the spectra of complexes of the type (1,2-diimine)M^{II}(1,2-ethylenedithiolate) with M = Ni, Pd, Pt (refs. 7, 8) and related complexes (refs. 9, 10). The diimine with its empty π orbitals is here the electron acceptor while the dithiolate acts as donor. LLCT transitions can be also identified in the spectra of complexes containing the same ligand in an oxidized and reduced form. $[Ru^{II}(bipy)_3]^+$ is apparently composed of two bipy ligands and one in its reduced state ($bipy^-$). The electronic spectrum of this complex displays a $bipy^-$ to bipy LLCT band in the near IR (ref. 11). A photoreaction originating from a LLCT state was reported recently (ref. 7).

Intra Ligand Charge Transfer (ILCT)

A ligand itself may consist of a reducing and an oxidizing part. The spectrum of the metal complex as well as that of the free ligand should show low-energy ILCT bands. An example of an optical ILCT transition is indeed known (ref. 12).

Metal to Metal Charge Transfer (MMCT)

Ligand-bridged binuclear (or polynuclear) complexes which contain a reducing and an oxidizing metal are characterized by optical MMCT transitions at low energies (refs. 4, 13-19). There are several well-documented examples of photochemical reactions induced by intramolecular MMCT excitation (ref. 19). In the first part of this review they are discussed in some detail as typical cases of photoredox processes initiated by optical CT transitions between weakly interacting redox sites.

A light-induced electron transfer involving weakly coupled redox centers

cannot only take place by direct optical CT excitation (resonance transfer). As a second possibility an intramolecular excited state electron transfer may occur (non-resonance transfer). This process does not require the presence of CT absorptions. The initial internal excitation of an electron donor or acceptor can be followed by electron transfer. Examples of this type are elaborated in the second part of this review.

The further discussion is essentially restricted to systems which are subject to a permanent photochemical change. However, reference is also made to complexes which undergo a reversible intramolecular electron transfer. In these cases the occurence of electron transfer was detected by emission or time-resolved absorption spectroscopy.

2 RESONANCE ELECTRON TRANSFER BY OPTICAL MMCT EXCITATION

The electronic coupling of metallic redox centers in binuclear complexes has been studied extensively for many years (refs. 13-18). The theory advanced by N. S. Hush provides the basis for a discussion of this interaction (refs. 15, 16, 18, 20, 21). A binuclear ligand-bridged complex of the type M_{α}^{red}-L-M_{β}^{ox} is composed of the two mononuclear components M_{α}^{red}-L and L-M_{β}^{ox}. Besides the bridging ligand both metals are coordinated to other terminal ligands. The electronic spectrum of the binuclear complex consists of the superimposed spectra of the mononuclear components if the interaction between the reducing and oxidizing metal is weak. In addition, a new absorption band appears which belongs to the optical MMCT transition from the reducing to the oxidizing metal (refs. 13-19).

With increasing metal-metal interaction the individual components loose their identity. Finally, the valence orbitals of both metals are completely delocalized and the metals do not any more exist in well-defined ("trapped") oxidation states. As a consequence the spectral features of the mononuclear components are not any more apparent and MMCT bands do not occur. They are now replaced by electronic transitions involving orbitals which are delocalized between both metals. An analysis of this absorption band provides the information on the extent of delocalization α^2.

$$\alpha^2 = \frac{4.24 \cdot 10^{-4} \cdot \varepsilon_{max} \cdot \Delta\bar{\nu}_{1/2}}{\bar{\nu}_{max} \cdot d^2}$$

The parameters are the energy of the MMCT band at its maximum $\bar{\nu}_{max}$, the molar extinction coefficient ε_{max}, the half-width of the MMCT band $\Delta\bar{\nu}_{1/2}$ and the metal-metal distance d. At complete delocalization α^2 is unity while the valencies are trapped if α^2 is much smaller than unity. Only in the latter case MMCT transitions are associated with a complete electron

transfer from one metal to another. The following discussion is restricted to this type of CT interaction.

The energy of the optical MMCT transition depends on the potential difference ΔE between the redox couples $M_\alpha^{red/ox}$ and $M_\beta^{red/ox}$ and on the reorganizational energy χ.

$$\tilde{\nu}_{max} = \Delta E + \chi$$

The parameter χ consists of an outer- and an inner-sphere contribution.

$$\chi = \chi_o + \chi_i$$

While χ_i is an intrinsic property of the binuclear complex χ_o depends on the reorganization of solvent environment according to

$$\chi_o = e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d}\right)\left(\frac{1}{n^2} - \frac{1}{D}\right)$$

The parameters a_1 and a_2 are the radii of the coordination spheres of both metals, d is the metal-metal distance, n and D are the refractive index and the static dielectric constant of the solvent. This equation means simply that χ_o and hence the energy of the MMCT transition varies with the polarity of the solvent. Since the specific complexes discussed below were investigated only in aqueous solution details on the solvent dependence are not elaborated here.

The inner-sphere contribution to the reorganizational energy is a fraction of the Franck-Condon MMCT transition as shown in Fig. 1. It depends on the structural distortion which accompanies electron transfer. This reorganization which may be represented by changes of the metal-ligand bond length of one metal center varies with the oxidation state of this metal. Frequently reduction is associated with an extension of the metal-ligand distance.

The optical MMCT is a Franck-Condon transition which terminates in a vibrationally excited state of the redox isomer $M_\alpha^{ox}/M_\beta^{red}$ before it relaxes. The electron transfer cannot only be achieved by light absorption but also as a thermal process which requires the activation energy E_{th} to reach the crossing point of both potential curves. When the redox isomer exists in its vibrational ground state it may undergo a thermal back electron transfer by overcoming the activation barrier E'_{th}.

The majority of compounds which were investigated with regard to optical MMCT transitions are homobinuclear complexes containing one metal in two different oxidation states. Particularly Ru^{II}/Ru^{III} systems found much attention (refs. 13-17). These complexes are called mixed-valence (MV) compounds. In this case the term MMCT is also known as intervalence transfer (IT). The potential curves (Fig. 1) of both redox isomers of such a symmetric MV complex are located at the same energy. They are only displaced

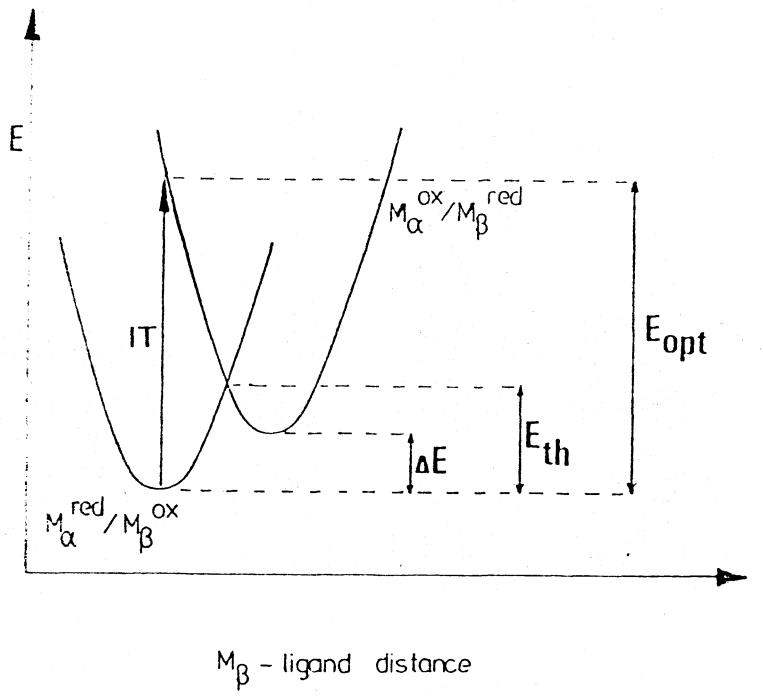

Fig. 1. Potential energy versus metal-ligand bond length for binuclear complexes containing a reducing and an oxidizing metal

horizontally due to the structural reorganization which accompanies the electron transfer. Unfortunately, for a variety of reasons these compounds are not well suited to observe a photochemical reaction leading to a permanent chemical change. First of all, in a symmetric MV complex an electron exchange does not cause a real chemical change, although the individual metal atoms have exchanged their oxidation state and hence their environment. But even in most homobinuclear complexes which are slightly asymmetric due to different ligands a rapid thermal electron exchange occurs. This situation interferes with the observation of light-induced electron transfer. Finally, the MMCT bands of the symmetric or nearly symmetric MV systems appear in the near IR which is not easily accessible by conventional irradiation sources and light detection devices. Consequently, photoactive systems should be designed according to these considerations.

Light-sensitivity will be most easily observed for strongly asymmetric binuclear complexes. They may be stable towards thermal electron exchange

which requires the activation energy E_{th} and are expected to display their MMCT bands in the visible or UV region (see Fig. 1). An asymmetric system may be constructed in two ways. In homobinuclear complexes different ligands at both metals can be employed. For example, in a Ru^{II}, Ru^{III} complex a large redox asymmetry will be achieved if Ru^{II} is stabilized by π-acceptor ligands and Ru^{III} by π-donors. Much larger energy separations are possible in heteronuclear systems. The individual components are selected according to their redox potentials.

Another very important criterion for a proper choice is the anticipated reactivity of the redox isomer generated by MMCT excitation. It will not be stable but return rapidly to the starting point since the activation barrier E'_{th} for back electron transfer is rather low (Fig. 1). An irreversible formation of stable photoproducts can only be achieved if the redox isomer is able to undergo some further geometrical rearrangements. These secondary processes must be fast enough to compete with back electron transfer. For example, photoactivity is expected if $[Co(NH_3)_6]^{3+}$ is the oxidizing component of a binuclear complex. Upon reduction $[Co(NH_3)_6]^{2+}$ is formed. It is kinetically very labile and undergoes a rapid decomposition in aqueous solution. According to these considerations in 1975 we started to explore photochemical reactions induced by MMCT excitation (refs. 19, 22, 23).

$[(NC)_5Ru^{II}CNCo^{III}(NH_3)_5]^-$

The binuclear cyanide-bridged complex $[(NC)_5RuCNCo(NH_3)_5]^-$ (ref. 22) may be viewed as being composed of $[Co^{III}(NH_3)_6]^{3+}$ and $[Ru^{II}(CN)_6]^{4-}$ if the coupling between Ru and Co is weak. The assumption that $[Co(NH_3)_6]^{3+}$ can be considered as one of the components is supported by the observation that bridging cyanide which coordinates via nitrogen is similar to ammonia with regard to its ligand field strength. Weak coupling is then indicated by the absorption spectrum of $[(NC)_5RuCNCo(NH_3)_5]^-$ which is indeed composed of the spectra of $[Ru(CN)_6]^{4-}$ and $[Co(NH_3)_6]^{3+}$ (Fig. 2). The binuclear complex displays its longest-wavelength absorption at λ_{max} = 475 nm. This is the first ligand field (LF) band of $[Co(NH_3)_6]^{3+}$. The other component $[Ru(CN)_6]^{4-}$ does not absorb above 300 nm. Independent support for a weak interaction of both metals comes from the IR spectrum. Beside the bridging cyanide which absorbs at 2135 cm^{-1} the stretching vibration of the terminal cyanides appears at 2050 cm^{-1}. This is the same value as that of $[Ru(CN)_6]^{4-}$. It follows that the oxidation state of ruthenium is two in the binuclear complex since the frequency of this stretching vibration is a sensitive function of the valency of the metal.

The presence of the reducing Ru^{II} and oxidizing Co^{III} leads to the appearance of a new absorption (Fig. 2) at λ_{max} = 375 nm (ε = 690) which is

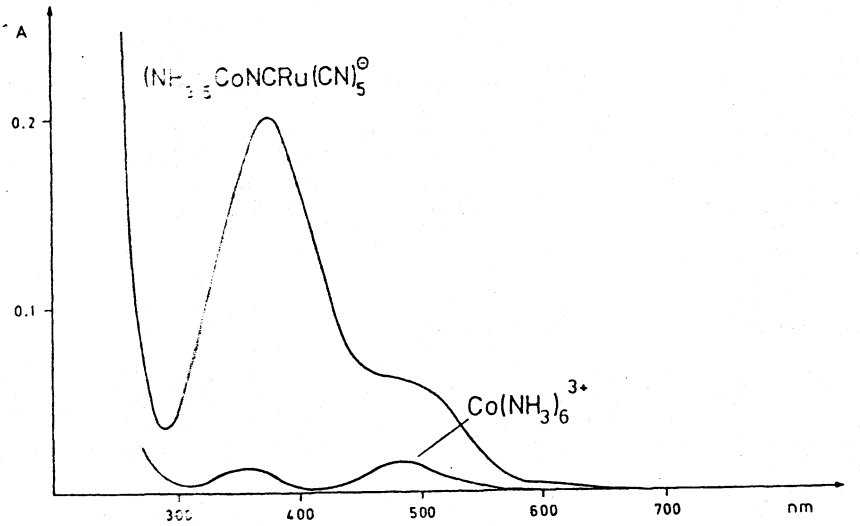

Fig. 2. Absorption spectra of aqueous $3x10^{-4}$ M $[(NH_3)_5CoNCRu(CN)_5]^-$ and $3x10^{-4}$ M $[Co(NH_3)_6]^{3+}$ at room temperature, 1-cm cell

assigned to a MMCT transition (ref. 22). An analysis of the band with regard to the Hush theory would require the knowledge of the potentials of the redox couples $Co^{III/II}$ and $Ru^{II/III}$ within the binuclear complex. These potentials are not known. However, for a very rough estimate the potentials of the mononuclear components $[Co(NH_3)_6]^{3+/2+}$ (E° = 0.11 V) (ref. 24) and $[Ru(CN)_6]^{4-/3-}$ (E° = 0.86 V) (ref. 24) may be taken. This gives a reorganizational energy of χ = 59 kcal/mol. Such a large value is certainly associated with the fact that the MMCT transition leads to the population of an antibonding e_g orbital of Co^{III} (in O_h symmetry) which causes a large distortion at Co^{II} in the redox isomer $[(NC)_5Ru^{III}CNCo^{II}(NH_3)_5]^-$. The activation barrier for thermal electron transfer from Ru^{II} to Co^{III} is then calculated to be E_{th} = 25 kcal/mol. Aqueous solutions of the binuclear complex are stable at room temperature but undergo a redox decomposition upon light absorption by the MMCT band with the quantum yield Φ = 0.46 at λ_{irr} = 366 nm.

$$[(NC)_5Ru^{II}CNCo^{III}(NH_3)_5]^- \xrightarrow{h\nu} [(NC)_5Ru^{III}CNCo^{II}(NH_3)_5]^-$$

$$[(NC)_5Ru^{III}CNCo^{II}(NH_3)_5]^- \rightarrow [Ru^{III}(CN)_6]^{3-} + Co^{2+} + 5\ NH_3$$

Because of the strong distortion of the vibrationally relaxed MMCT state, thermal back electron transfer is now associated with a substantial activation barrier of E'_{th} = 5 kcal. The decomposition of the kinetically labile Co^{II} is apparently fast enough to compete with charge recombination.

An attempt to prepare the corresponding binuclear iron complex $[(NH_3)_5Co^{III}NCFe^{II}(CN)_6]^-$ failed. Upon mixing solutions of $[Co(NH_3)_5H_2O]^{3+}$ and $[Fe(CN)_6]^{4-}$ a rapid thermal outer-sphere electron transfer from Fe(II) to Co(III) takes place (ref. 25) before the formation of the binuclear complex occurs. $[Fe(CN)_6]^{4-}$ ($E° = 0.36$ V vs SCE) is more reducing than $[Ru(CN)_6]^{4-}$ by 0.5 V (ref. 24). Assuming the same reorganizational energy of χ = 58 kcal/mol for both binuclear complexes $[(NH_3)_5Co^{III}NCM^{II}(CN)_5]^-$ with M = Fe and Ru the activation barrier would now be only E_{th} = 17 kcal/mol for thermal electron transfer within the hypothetical complex $[(NH_3)_5Co^{III}NCFe^{II}(CN)_5]^-$ in an aqueous solution.

$\underline{[(NC)_5Fe^{II}CNCr^{III}(NH_3)_5]^-}$

The binuclear ion $[(NC)_5Fe^{II}CNCr(NH_3)_5]^-$ consists of the components $[Fe^{II}(CN)_6]^{4-}$ and $[Cr(NH_3)_6]^{3+}$ which are weakly coupled (ref.26). The MLCT band of $[Fe(CN)_6]^{4-}$ at λ_{max} = 210 nm can be recognized in the spectrum of the binuclear complex. The typical LF bands of $[Cr(NH_3)_6]^{3+}$ are apparently obscured by the much more intense absorption at λ_{max} = 376 nm (ε = 2400) which is assigned to the MMCT transition from the reducing Fe^{II} to the oxidizing Cr^{III}.

The potential difference between the redox couples $[Fe(CN)_6]^{4-/3-}$ and $[Cr(NH_3)_6]^{3+/2+}$ is ΔE = 1.19 V. Taking this as a rough estimate for ΔE of the binuclear complex the electron transfer is associated with a reorganizational energy of χ = 49 kcal. This large value supports the assumption that the antibonding e_g orbitals at Cr(III) (in O_h symmetry) are the acceptor orbitals of the MMCT transition. The binuclear complex is quite stable in aqueous solution with regard to thermal electron transfer (E_{th} = 29 kcal) while an efficient photolysis takes place upon MMCT excitation (Φ = 0.1 nm at λ_{irr} = 366 (ref. 26):

$$[(NC)_5Fe^{II}CNCr^{III}(NH_3)_5]^- \xrightarrow{h\nu} [(NC)_5Fe^{III}CNCr^{II}(NH_3)_5]^-$$

$$[(NC)_5Fe^{III}CNCr^{II}(NH_3)_5]^- \rightarrow [Fe^{III}(CN)_6]^{3-} + Cr^{2+} + 5\ NH_3$$

The Franck-Condon state reached by the optical MMCT transition undergoes a rapid vibrational relaxation to the thermally equilibrated redox isomer Fe^{III}/Cr^{II}. The large distortion at Cr^{II} slows down back electron transfer ($E'_{th} \approx 2$ kcal). The kinetically labile Cr^{II} undergoes a ligand displacement before charge recombination can occur. Finally, Cr^{2+} is oxidized by oxygen.

$[(NC)_5M^{II}CNCo^{III}(CN)_5]^{6-}$ with M = Fe, Ru, and Os

The IR spectra of the anions $[(NC)_5M^{II}CNCo^{III}(CN)_5]^{6-}$ (refs. 23, 26) with M = Fe, Ru, and Os are indicative of weak coupling between M^{II} and Co^{III}. The absorptions of the terminal cyanides appear at nearly the same wavenumbers as those of mononuclear cyano complexes of M^{II} and Co^{III}. The electronic spectra of the binuclear complexes are less instructive since well-separated bands do not appear. However, there is much evidence that the absorption features at λ_{max} 385 nm (ϵ = 630) for M = Fe, 312 nm (460) for Ru, and 360 nm (734) for Os can be assigned to MMCT transitions from M^{II} to Co^{III} (refs. 23, 26). The energy of the MMCT band varies with the reducing strength of $[M(CN)_6]^{4-}$ (M = Fe, E° = +0.36 V; Ru 0.86 V and Os 0.56 V) (refs. 24, 27).

The MMCT transitions of the binuclear complexes terminate in e_g orbitals of Co^{III}. The thermally equilibrated redox isomers $[(NC)_5M^{III}CNCo^{II}(CN)_5]^{6-}$ are expected to undergo large distortions at Co^{II}. Reorganizational energies of more than 45 kcal are estimated.

All three anions $[(NC)_5M^{II}CNCo^{III}(CN)_5]^{6-}$ are stable in solution (refs. 23, 26). The activation energies for thermal electron transfer may exceed 30 kcal. However, in all cases the aqueous complexes undergo photoredox reactions upon MMCT excitation. The redox isomers $[(NC)_5M^{III}CNCo^{II}(CN)_5]^{6-}$ dissociate in the primary photochemical step:

$$[(NC)_5M^{II}CNCo^{III}(CN)_5]^{6-} \xrightarrow{h\nu} [(NC)_5M^{III}CNCo^{II}(CN)_5]^{6-}$$

$$[(NC)_5M^{III}CNCo^{II}(CN)_5]^{6-} \rightarrow [M^{III}(CN)_6]^{3-} + [Co^{II}(CN)_5]^{3-}$$

In the absence of oxygen a complete regeneration of the binuclear complexes occurs by a thermal inner-sphere electron transfer which is simply a reversal of the photoreaction. The activation barrier for this back electron transfer was estimated to be around E'_{th} = 2 kcal. The regeneration of the binuclear complexes by this inner-sphere redox process is not surprising since all three cyanide-bridged anions are synthesized by this reaction. The iron complex was prepared by Haim and Wilmarth in 1961 according to this procedure (ref. 28). In distinction to ammine complexes of Co^{II} which decay irreversibly in aqueous solution the complex $[Co^{II}(CN)_5]^{3-}$ does not decompose.

The photolysis of all three complexes induced by MMCT excitation leads to a permanent chemical change only in the presence of air. The complex $[Co(CN)_5]^{3-}$ can be intercepted by O_2:

$$2[Co(CN)_5]^{3-} + O_2 \rightarrow [(NC)_5Co^{III}(O_2^{2-})Co^{III}(CN)_5]^{6-}$$

In acidic solution the peroxo complex decomposes to yield H_2O_2 and $2[Co^{III}(CN)_5(H_2O)]^{2-}$ while in basic solution the peroxo complex is

further oxidized to the superoxo complex $[(NC)_5Co^{III}(O_2^-)Co^{III}(CN)_5]^{5-}$. The quantum yields for the formation of $[M^{III}(CN)_6]^{3-}$ are slightly wavelength-dependent due to the overlap of the MMCT bands with absorptions of other origin. The quantum yields may exceed unity because $[M(CN)_6]^{3-}$ is not only produced in the primary photochemical reaction but also by the oxidation of $[M(CN)_6]^{4-}$ by H_2O_2. The quantum yields are fairly large: $\Phi = 1.6$ at $\lambda_{irr} = 405$ nm for M = Fe; $\Phi = 0.39$ at $\lambda_{irr} = 313$ nm for M = Ru, and $\Phi = 0.32$ at $\lambda_{irr} = 366$ nm for M = Os (refs. 23, 26).

3 EXCITED STATE (NON-RESONANCE) ELECTRON TRANSFER

3.1 Introduction

A photoinduced electron transfer does not only occur by direct optical excitation (resonance transfer). As an alternative an electronically excited molecule may undergo an electron transfer to or from another molecule. Intermolecular excited state electron transfer of this type has been studied intensively (refs. 14, 29, 30). Particularly the complex $[Ru(bipy)_3]^{2+}$ was used as excited state electron donor or acceptor (ref. 31). In solution intermolecular electron transfer can take place if the excited molecule has a diffusional encounter with a suitable redox partner before it returns to the ground state.

An excited state electron transfer may take place also as intramolecular process. An excited chromophoric group can undergo an electron transfer to or from another part of the same molecule. Since donor and acceptor are already in contact prior to electronic excitation a long lifetime of the excited state is not required. Even higher excited states which can not participate in bimolecular reactions due to their short lifetimes may undergo intramolecular electron transfer. While in bimolecular redox processes the structural arrangement of donor and acceptor in the encounter complex is not known intramolecular electron transfer occurs in a better defined environment. Although these features make it attractive to study intramolecular excited state electron transfer this subject has been largely neglected until a few years ago.

The recent interest in intramolecular excited state electron transfer is associated with attempts to understand the primary events of photosynthesis and to design model systems for the photosynthesis (ref. 32). In the first step an excited state electron transfer occurs which must be uphill with regard to the ground state in order to convert light into chemical energy. In simple systems this first step is followed by a rapid downhill charge recombination. In the photosynthesis a charge separation is achieved by introducing a barrier for back electron transfer. Recently model compounds have been designed to study the charge separation in detail. A system which found much attention consists of a porphyrin as excited state electron donor which is linked covalently to a qui-

none as electron acceptor. In addition, a carotene may be attached as a donor to accomplish charge separation over large distances (ref. 32). However, in this review the discussion is restricted to typical transition metal complexes.

Two different cases will be distinguished. First, the primary electron transfer is followed by rapid secondary processes which compete successfully with back electron transfer. As a result, the light absorption leads to a permanent chemical change. Secondly, charge recombination is rapid and a net photolysis is not observed. Luminescence and time-resolved absorption spectroscopy were applied to gain insight into the charge separation and recombination processes.

The compounds discussed below do not display CT absorption bands involving the electron donor and acceptor. In some cases this is a good indication that electronic coupling is weak. In other cases the extent of coupling is more difficult to assess since CT bands of interest may be obscured by absorptions of different origin.

3.2 IRREVERSIBLE PHOTOREDUCTION OF Co(III)

3.2.1 Aromatic Molecules as Electron Donors

In 1969 Adamson et al. observed a photoreduction of Co^{III} upon IL excitation of aqueous $[Co^{III}(NH_3)_5TSC]^{2+}$ with TSC^- = trans-4-stilbene-carboxylate (ref. 33). In a later study a detailed analysis of the photoredox products of this complex was carried out (ref. 34).

The stilbene moiety is an isolated chromophore of the complex since its absorption spectrum did not change upon coordination via the carboxylic group. Any bands which could be assigned to a CT transition from the stilbene group to Co^{III} do not appear.

The photolysis takes place according to the following reaction scheme (* excited state):

$$[Co^{III}(NH_3)_5(TSC^-)]^{2+} \xrightarrow{h\nu} [Co^{III}(NH_3)_5(TSC^-)^*]^{2+}$$

$$[Co^{III}(NH_3)_5(TSC^-)^*]^{2+} \rightarrow [Co^{II}(NH_3)_5(TSC^0)]^{2+}$$

$$[Co^{II}(NH_3)_5(TSC^0)]^{2+} \rightarrow Co^{2+} + 5NH_3 + TSC^0$$

$$[Co^{III}(NH_3)_5(TSC^-)]^{2+} + TSC^0 \rightarrow Co^{2+} + 5NH_3 + TSC^- + \text{oxid. TSC}$$

$$TSC^0 + O_2 \rightarrow \text{benzaldehyde + other products}$$

Upon light absorption at 313 nm the first excited $\pi\pi^*$ singlet of the TSC^- ligand is populated. This IL state is strongly reducing ($E_{1/2} \approx -2$ V vs SCE) while the Co^{III} center is a weak oxidant ($E_{1/2} = -0.03$ V) (ref. 35). Excited state electron transfer from the IL state of the stilbene group to Co^{III} has obviously a large driving force and is apparently very rapid. While the free ligand shows a strong fluorescence and undergoes a trans/cis

photoisomerization these processes are not observed in the coordinated state. The electron transfer is thus much faster than other deactivation processes of the ππ* singlet. In the original study (ref. 33) it was suggested that the excited IL state undergoes an energy transfer to a non-spectroscopic LMCT excited state of the complex. This explanation seems to be equivalent to an excited state electron transfer if the LMCT state can be described as a stilbene radical cation coordinated to Co^{II} by a carboxylic group (ref. 34).

The Co^{II} complex generated by excited state electron transfer is kinetically labile and decomposes before an efficient charge recombination takes place. A TSC radical is released and undergoes further reactions according to the scheme (ref. 34).

Interestingly, the lowest ππ* triplet of the TSC^- ligand which can be populated by intermolecular energy transfer from biacetyl and other sensitizers induces only the trans/cis isomerization of the ligand but not the reduction of Co^{III} (ref. 34). The redox potential of the IL triplet is only $E_{1/2} \approx -0.3$ V vs SCE. Electron transfer is now apparently not fast enough to compete with other deactivation processes such as the photoisomerization.

A variety of other complexes of the type $[Co^{III}(NH_3)_5OOCR]^{2+}$ with R = aromatic group such as 1- and 2-naphthalene, 9-anthracene, 4-biphenyl shows qualitatively the same behavior as the TSC complex (refs. 37, 38). The quantum yields of Co^{2+} production was dependent very much on the nature of R. A simple correlation was not apparent.

The complexes [2-naphthyl-CONH-$(CH_2)_n$-$COOCo^{III}(NH_3)_5]^{2+}$ with n = 1-5 were studied in order to learn more about the structural requirements for excited state electron transfer (ref. 39). The naphthyl group as excited state donor and Co^{III} as acceptor are connected by a peptide linkage. In distinction to the complexes discussed above Co^{III} and the aromatic group are now not only separated by a carboxylic group but also by saturated and hence electronically insulating methylene groups. The basic observations were the same as those for the related complexes without intervening CH_2 groups. However, additional data were obtained since fluorescence quenching of the naphthyl moiety by Co^{III} was efficient but not complete. The observations can be described by the following reaction scheme (N = 2-naphthyl, B = peptide bridge):

$$[N\text{-}B\text{-}Co^{III}(NH_3)_5]^{2+} + h\nu \rightarrow [N^*\text{-}B\text{-}Co^{III}(NH_3)_5]^{2+}$$

$$[N^*\text{-}B\text{-}Co^{III}(NH_3)_5]^{2+} \xrightarrow{k_1} [N\text{-}B\text{-}Co^{III}(NH_3)_5]^{2+} + h\nu$$

$$[N^*\text{-}B\text{-}Co^{III}(NH_3)_5]^{2+} \xrightarrow{k_2} [N\text{-}B\text{-}Co^{III}(NH_3)_5]^{2+} + \text{heat}$$

$$[N^{*}\text{-B-}Co^{III}(NH_3)_5]^{2+} \xrightarrow{k_3} [N^{+}\text{-B-}Co^{II}(NH_3)_5]^{2+}$$

$$[N^{+}\text{-B-}Co^{II}(NH_3)_5]^{2+} \xrightarrow{k_4} [N\text{-B-}Co^{III}(NH_3)_5]^{2+}$$

$$[N^{+}\text{-B-}Co^{II}(NH_3)_5]^{2+} \xrightarrow{k_5} Co^{2+} + 5\ NH_3 + \text{oxid. N}$$

The $\pi\pi^{*}$ singlet of the naphthyl group is populated by irradiation with λ = 313 nm. The excited singlet of the free ligand has a lifetime of approximately 10^{-8} s and undergoes an efficient fluorescence, which is strongly quenched in the complex due to electron transfer to Co^{III}. From the relative quantum yields of fluorescence the rate constants k_3 and quantum yields Φ_{ET} of excited state electron transfer were obtained. An increase from $k_3 = 4.9\times10^{9}\ s^{-1}$ and $\Phi_{ET} = 0.98$ for n = 1 to $9.2\times10^{9}\ s^{-1}$ and 0.99 for n = 4 was observed. At n = 5 k_3 and Φ_{ET} dropped to $6.0\times10^{9}\ s^{-1}$ and 0.98.

From Φ_{ET} and the experimental quantum yields of Co^{2+} formation relative rate constants for back electron transfer k_4^{i} were calculated assuming that the rate of Co^{2+} formation k_5 is independent of n. It was found that the rate of back electron transfer reached also a maximum at n = 4.

On the basis of these results it is concluded that the actual distance of excited state and back electron transfer decreases with increasing chain length of the peptide from n = 1 to 4.

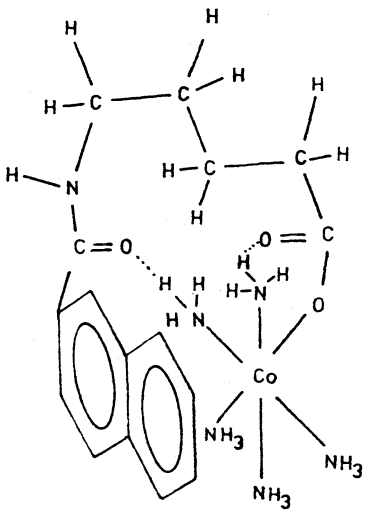

Fig. 3. Suggested structure of aqueous [2-naphthyl-CONH-$(CH_2)_4$-$COOCo^{III}$-$(NH_3)_5]^{2+}$

It is assumed that donor and acceptor come to a closer approach by an appropriate bending of the flexible peptide linkage. This back folding may be favored by hydrogen bonding between coordinated ammonia and carbonyl groups of the peptide (Fig. 3). At n = 5 electron transfer becomes less efficient. The donor-acceptor distance may now increase by an extension of the peptide.

Finally, it should be mentioned here that excited state electron transfer from an aromatic molecule to Co(III) ammines takes place also as an intermolecular reaction (refs. 38, 40). First observations were explained by the assumption that an energy transfer occurs to reactive LMCT states of the complex (ref. 40). However, more recent investigations have shown that the aromatic molecules are indeed oxidized and all observations can be explained best by an excited state electron transfer mechanism (ref. 38).

3.2.2 Metal Complexes as Electron Donors

Intramolecular excited state electron transfer between weakly coupled redox centers takes also place in complexes of the type

$$[(NH_3)_5Co^{III}NH_2\text{-}(CH_2)_n\text{-}CH{=}CH_2Cu^{I}]^{4+}$$

The Cu^{I} olefin π-complex is now an isolated chromophore which is characterized by an optical Cu^{I} to π^*(olefin) MLCT transition (ref. 41). The interaction of this chromophore with Co is certainly weak due to the intervening saturated methylene groups. Light absorption by the Cu^{I} olefin chromophore is followed by the reduction of Co^{III} and oxidation of Cu^{I}. In aqueous solution stable redox products are formed according to the equation:

$$[(NH_3)_5Co^{III}NH_2\text{-}(CH_2)_n\text{-}CH{=}CH_2Cu^{I}]^{4+} \rightarrow Co^{2+} + Cu^{2+} + 5NH_3 + NH_2\text{-}(CH_2)_n\text{-}CH{=}CH_2$$

The MLCT state of the copper complex acts here as excited state electron donor. In the excited state it is the reduced olefin which undergoes electron transfer to Co^{III}:

$$\{(NH_3)_5Co^{III}\text{-}NH_2\text{-}(CH_2)_n\text{-}[(CH{=}\dot{C}H_2)Cu^{II}]^*\}^{4+} \rightarrow [(NH_3)_5Co^{II}\text{-}NH_2\text{-}(CH_2)_n\text{-}CH{=}CH_2Cu^{II}]^{4+}$$

The electron transfer to Co^{III} is fast enough to compete with internal deactivation in the copper complex. The rate constant for electron transfer was estimated by time-resolved absorption spectroscopy to be $k > 10^7\text{-}10^8$ s^{-1}. Finally, the kinetically labile Co^{II} complex undergoes a ligand displacement. The quantum yield of Co^{2+} formation decreases with an increasing number n of CH_2 groups. Beyond four to five methylene groups electron transfer is no longer competitive with internal deactivation within the Cu chromophore. The actual distance between donor and acceptor seems here to increase with the length of the connecting CH_2 chain. At a fully extended

chain a maximum distance of about 7 Å for electron transfer was estimated.

Similar observations were made with binuclear Co^{III}/Cu^{I} complexes which contain a pyridine or carboxylic group instead of an amine coordinated to Co^{III} (ref. 41).

Intramolecular excited state electron transfer from a metal complex as donor to Co^{III} as acceptor occurs also in the neutral complex:

$[(NC)_5Fe^{II}pyrazineCo^{III}(NH_3)_5]$

This binuclear compound is composed of the chromophore $[Fe^{II}(CN)_5pyrazine]^{3-}$ and $[Co^{III}(NH_3)_5pyrazine]^{3+}$ (ref. 42). The metal centers do not seem to be strongly coupled. The iron containing chromophore is characterized by an optical Fe^{II} to π^*(pyrazine) MLCT transition (λ_{max} = 630 nm).

Upon light absorption into this CT band an efficient reduction of Co^{III} took place according to the equation:

$$[(NC)_5Fe^{II}pyrazineCo^{III}(NH_3)_5] \xrightarrow{h\nu} [Fe^{III}(CN)_5pyrazine]^{2-} + Co^{2+} + 5NH_3$$

The processes following light absorption should be quite analogous to those of the Co^{III}/Cu^{I} complex described above. The MLCT excited state of the iron chromophore transfers an electron from the reduced pyrazine bridge to Co^{III} before it undergoes an internal deactivation.

Interestingly, the complex $[(NC)_5Fe^{III}pyrazineCo^{II}(NH_3)_5]$ which is the primary product of the electron transfer is a Fe^{II} to Co^{III} MMCT state or redox isomer of the starting complex. This MMCT state lies certainly well below the Fe to pyrazine MLCT state. The excited state electron transfer can then be also considered as an energy transfer from a MLCT to a MMCT excited state. In the absorption spectrum of the binuclear Fe^{II}/Co^{III} complex a MMCT band was not identified. However, it may be obscured by the MLCT absorption. It is also possible that a MMCT band appears in the near IR region which may have not been investigated. The expectation that a MMCT state occurs at rather low energies is supported by another observation. This MMCT state can be populated even thermally. The redox decomposition of the binuclear complex does not take place only as a photoreaction but also as a thermal process (ref. 42). Analogous results were obtained with binuclear Fe^{II}/Co^{III} complexes which contain bridging ligands similar to pyrazine (ref. 42).

3.3 Reversible Excited State Electron Transfer

3.3.1 Introduction

Intramolecular excited state electron transfer between weakly coupled redox centers described in the previous section results in a permanent chemi-

cal change. In addition, there are many systems which undergo an efficient back electron transfer regenerating the starting compound. These materials appear to be not light-sensitive. However, by means of time-resolved absorption or emission spectroscopy it is possible to demonstrate the existence of short-lived intermediates. Many of such studies were carried out in order to get more information on the charge separation process. It was assumed that back electron transfer could be retarded if the electron/hole pair can be separated over increased distances. However, this may not always be true. In suitable cases through-bond interaction seems to provide some coupling of donor and acceptor which may facilitate an efficient charge recombination over larger distances. This assumption is supported by recent observations that optical CT transitions occur also between remote redox centers. The spectrum of $[(NH_3)_5Ru^{II}pyrazineRu^{II}(NH_3)_4pyrazineRu^{III}(NH_3)_5]^{7+}$ displays a near-IR absorption which was assigned to an end-to-end MMCT transition (ref. 43). An absorption band of the ion $[(NH_3)_5Ru^{II}NCRu^{II}(bipy)_2CNRu^{II}(NH_3)_4]^{4+}$ was identified as MLCT transition from Ru^{II} coordinated to ammonia to bipy of the adjacent ruthenium atom (ref. 44). As a further example M^{II} to bipy MLCT bands were detected in the spectra of $[(bipy)(H_2O)Pt^{II}NCM^{II}(CN)_4CNPt^{II}(H_2O)(bipy)]$ with M = Fe, Ru, and Os (ref. 45).

In the following discussion of reversible intramolecular excited state electron transfer individual complexes are presented. They are classified according to the donor and acceptor site of excited state electron transfer following directly optical excitation of one chromophore. Evidence of this primary excited electron transfer was obtained by the identification of subsequent slower processes.

3.3.2 Ligand to Metal Electron Transfer

In the binuclear ion $[(NH_3)_5Ru^{II}pyrazineCu^{II}(aq)]^{4+}$ the optical MLCT transition generates the excited state $[(NH_3)_5Ru^{III}(pyrazine^-)Cu^{II}]^{4+*}$ (ref. 46). This is followed by a rapid electron transfer from the reduced bridging ligand to Cu^{II} producing $[(NH_3)_5Ru^{III}pyrazineCu^{I}]^{4+}$ which undergoes regeneration of the starting complex. The metal-to-metal back electron transfer takes place with a first order rate constant of $k = 7.8 \times 10^3\ s^{-1}$.

The mixed-valence compound $[(NH_3)_5Ru^{II}pyrazineRu^{III}(edta)]^+$ can be excited to $[(NH_3)_5Ru^{III}(pyrazine^-)Ru^{III}(edta)]^{+*}$ by light absorption into the corresponding MLCT band (ref. 47). In this excited state electron transfer takes place from the reduced pyrazine ligand to Ru^{III} coordinated to edta with $k > 10^{11}\ s^{-1}$. The complex $[(NH_3)_5Ru^{III}pyrazineRu^{II}(edta)]^+$ which is a high-energy redox isomer of the ground state or a MMCT excited state regenerates the starting complex by metal-to-metal

electron transfer ($k = 0.8 \times 10^{10}\ s^{-1}$). Similar results were obtained with related mixed-valence compounds (ref. 47).

The complex $[(bipy)Re^{I}(CO)_3(py\text{-}PTZ)]^{+}$ contains a coordinated pyridine (py) which is linked at its 4 position to the reducing phenothiazine (PTZ) molecule via an insulating methylene group (ref. 48). An optical MLCT transition leads to the excited state $[(bipy^{-})Re^{II}(CO)_3(py\text{-}PTZ)]^{+*}$ which undergoes rapid excited state electron transfer from PTZ to the oxidized Re center. In contrast to the previous examples this electron transfer is not an inner-sphere process since the donor site is isolated by the intervening CH_2 group. The result of this excited state electron transfer is a LLCT excited state with the electron distribution $[(bipy^{-})Re^{I}(CO)_3(py\text{-}PTZ^{+})]^{+*}$. It reverts to the ground state with $k = 4 \times 10^{8}\ s^{-1}$.

3.3.3 Metal to Metal Electron Transfer

The binuclear ion $[(bipy)_2(CO)Os^{II}LOs^{II}(o\text{-}phen)(dppe)Cl]^{3+}$ with L = 4,4'-bipy and dppe = cis-$Ph_2PCH{=}CHPPh_2$ undergoes optical MLCT excitation to form $[(bipy)(bipy^{-})(CO)Os^{III}LOs^{II}(o\text{-}phen)(dppe)Cl]^{3+*}$ which is a mixed-valence compound existing only in the excited state (ref. 49). The optical transition is followed by an excited state metal-to-metal electron transfer from Os^{II} to Os^{III} with $k \approx 10^{7}\ s^{-1}$ yielding $[(bipy)(bipy^{-})(CO)\text{-}Os^{II}LOs^{III}(o\text{-}phen)(dppe)Cl]^{3+}$. Subsequent electron transfer from $bipy^{-}$ to the remote Os^{III} regenerates the stable ground state.

In the heterobimetallic cation $[(bipy)_2Ru^{II}bipymRe^{I}(CO)_3Cl]^{2+}$ with bipym = 2.2'-bipyrimidine an optical MLCT transition terminates in the excited state $[(bipy)_2Ru^{II}(bipym^{-})Re^{II}(CO)_3Cl]^{2+*}$ (ref. 50). This MLCT state undergoes metal-to-metal electron transfer from Ru^{II} to the oxidized rhenium to form $[(bipy)_2Ru^{III}(bipym^{-})Re^{I}(CO)_3Cl]^{2+*}$. The production of this MLCT excited state was detected by its emission to the ground state.

3.3.4 Ligand to Ligand Electron Transfer

The complexes $[(bipy)_2Ru^{II}(MeQ^{+})_2]^{4+}$ (ref. 51) and $[(bipy)Re^{I}\text{-}(CO)_3(MeQ^{+})]^{2+}$ (ref. 52) contain the oxidizing ligand NCH_3-4.4'-bipyridinium cation (MeQ^{+}) which is weakly coupled to the metals. The optical transition to the MLCT state involving the promotion of an electron from the metal to the bipy ligand is followed by the reverse process as emission but only at low temperatures in a rigid matrix. In fluid solution at room temperature the MLCT states $[(bipy)(bipy^{-})Ru^{III}(MeQ^{+})_2]^{4+*}$ and $[(bipy^{-})Re^{II}(CO)_3(MeQ^{+})]^{2+*}$ undergo excited state electron transfer from the reduced $bipy^{-}$ to the oxidizing MeQ^{+} ligand. This process generates the MLCT states $[(bipy)_2Ru^{III}(MeQ^{o})(MeQ^{+})]^{4+*}$ and $[(bipy)Re^{II}(CO)_3\text{-}(MeQ^{\circ})]^{2+*}$ which were identified by their emission spectra. The excited

state ligand-to-ligand electron transfer requires apparently an orientational mobility of the MeQ^+ ligand which is possible only in fluid solution. It was suggested that electron transfer can occur if both aromatic rings of MeQ^+ assume a coplanar arrangement. This assumption is supported by the observation that the complex $[(bipy)_2Os^{II}(CO)$(N,3,3'-trimethyl-4,4'-bipyridinium$^+$)$]^{3+}$ does not undergo this excited state ligand-to-ligand electron transfer (ref. 52). Due to a steric repulsion imposed by the methyl substituents in the 3 and 3' position of the MeQ^+ ligand a coplanar position of both rings cannot be adopted.

An excited state ligand-to-ligand electron transfer was also observed for the mixed-valence compound $[(dpte)_2ClRu^{II}LRu^{III}(bipy)_2Cl]^{3+}$ with dpte = 1,2-diphenylthioethane and L = 4,4'-bipyridine (refs. 53, 54). The optical transition from Ru^{II} to the bridging ligand L yields the MLCT state $[(dpte)_2ClRu^{III}(L^-)Ru^{III}(bipy)_2Cl]^{3+*}$. Excited state electron transfer generates another MLCT state $[(dpte)_2Ru^{III}LRu^{III}(bipy^-)$-$(bipy)Cl]^{3+*}$. This state which cannot be reached by an optical transition from the ground state was detected by its luminescence. The emission leads to a species with the electron distribution $[(dpte)_2ClRu^{III}LRu^{II}(bipy)_2Cl]^{3+}$. This is a MMCT excited state which is rapidly deactivated to the ground state. Similar results were obtained with analogous complexes containing other bridging ligands related to 4,4'-bipy.

CONCLUSION

A light-induced intramolecular electron transfer between weakly coupled redox centers involving transition metal complexes can take place by direct optical charge transfer excitation (resonance mechanism) as well as by excited state electron transfer (non-resonance mechanism). The primary charge-separated state undergoes competing back electron transfer and secondary transformations. The efficiency of the formation of stable photoproducts is determined by this competition. It depends on various factors such as the reorganizational energy and the extent of electronic coupling between electron donor and acceptor. More studies are needed to obtain a detailed picture. Structural requirements such as the distance and the angle between donor and acceptor but also the nature of the connecting bridge play an important role which is not yet completely understood. As a long-term goal an efficient charge separation which can be utilized in an artificial photosynthesis and other applications seems to be feasible.

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